## REMARKS

As requested, the amendment to the specification has been resubmitted to eliminate the partially blocked and illegible material.

The presence of internal electrode materials dispersed within a ceramic body have led to the deterioration of piezoelectric properties and poor reliability as attempts have been made to reduce the size of monolithic piezoelectric parts by reducing the thickness of the layer of the ceramic sheets which make up such parts and increasing the number of sheets. One such property is the piezoelectric d constant which relates the amount of mechanical strain produced by an applied electric field. In monolithic piezoelectric parts such as monolithic piezoelectric actuators, audio admitters, sensor and the like, a high constant is required.

It is recognized in the art that when the piezoelectric ceramic is a lead perovskite type material, the piezoelectric d constant is conspicuously deteriorated when sintering in a low oxygen atmosphere because the low oxygen concentration promotes the generation of oxygen pores. When the oxygen concentration is reduced to less than one percent by volume or when a soft piezoelectric ceramic material with a high piezoelectric d constant is used, the deterioration is so severe that it is difficult to even form the desired monolithic piezoelectric part.

The present invention is based, in part, on the discovery that a layered article which has a plurality of piezoelectric ceramic layers and spaced internal electrode layers disposed in the part can be fabricated without deteriorating the piezoelectric d constant by co-sintering the ceramic layers and internal electrode layers in an atmosphere where the oxygen concentration is up to about 5 volume percent, but not

zero percent, when the molar quantity of the A site of the perovskite has been reduced by about 0.5 to 5 mole percent from the stoichiometric amount, and the average valence of the B site component is increased to greater than 4 but less than 4.1. The fact that the deterioration of the constant can be combated is surprising and unexpected.

Claims 1, 4, 5, 7 and 14-16 were rejected under 35 U.S.C. 103 over Randall in view of Ponomarev and Horikawa '408. This rejection is respectfully traversed.

Randall teaches co-firing multi-layered piezoelectric ceramic materials with base metal electrodes. The reference acknowledges that there are significant problems with such co-firing, including, *inter alia*, firing without oxidation of the electrodes and also without reduction of the PZT or other ceramic material. See e.g. paragraph [0007]. Randall teaches that these problems can be overcome by applying a layer comprising an organic material, flux and a dopant to a piezoelectric ceramic layer, then applying a layer of a base metal powder coated with an inorganic passivation agent in an organic material, and then continuing application of these layers until the desired structure is achieved. The resulting structure is heated to remove the organic material and then sintered at a partial oxygen pressure of about $10^{-3}$ to $10^{-10}$. As the Examiner has acknowledged, Randall fails to teach or suggest using a perovskite ceramic whose A and B site molar quantities have been altered from the stoichiometric composition (i.e., $ABO_3$).

The Ponomarev reference has been cited solely to teach that low loss hard piezoelectric ceramic materials are desired in multi-layer ceramic transformers.

Horikawa '408 relates to low loss piezoelectric ceramics for high frequency filters and isolators. The ceramic has the particular composition given at column 2, lines 50 to 55 and is formed by preparing a ceramic molded body of the ceramic which

is sintered and thereafter processed for the application of electrodes.  There is no

teaching or suggestion in this reference of cofiring a green (unsintered) piezoelectric

ceramic with internal electrodes under any conditions.  In addition, there is no teaching

or suggestion that the ceramic should be fired in a reduced oxygen atmosphere for any

reason.  Accordingly,  Horikawa '408 did not have to face the problem of deterioration

of the d constant.

The rejection in this case is predicated on substituting the Horikawa '408

ceramic for the Randall ceramic based on the assertion that Ponomarev teaches a low

loss material would be advantageous.  Applicants have previously pointed out that this

approach ignores the fact that the prior art is well aware of the fact that sintering a lead

perovskite piezoelectric ceramic material in a reduced oxygen atmosphere causes a

significant deterioration in the piezoelectric d constant and can even render the sintered

ceramic unusable for its intended purpose.  Applicants have drawn the Examiner's

attention to the illustration of this fact in the comparative examples of Table 3 in the

present application.

The Examiner has taken issue based on the proposition that one would not

expect the ceramic to have deteriorated the piezoelectric d constant because Randall

clearly discloses that the piezoelectric ceramic can be sintered in a reducing atmosphere

without being reduced.  In response, Applicants respectfully submit that the Examiner

is equating, without any factual basis, reduction of the piezoelectric ceramic with

deterioration of the piezoelectric d constant.  However, a piezoelectric ceramic can be

sintered in a reducing atmosphere without being reduced at the same time the

piezoelectric d constant deteriorates.  In this connection, the Examiner will note that

Randall was not concerned about, and has no disclosure whatsoever about, the

piezoelectric d constant.  Attention is also respectfully invited to the article by Moon

and Jang, *Effects of Sintering Atmosphere on Densification Behavior and Piezoelectric Properties of $Pb(Ni_{1/3}Nb_{2/3})O_3$-$PbTiO_3$-$PbZrO_3$ Ceramics*, J. Am. Ceram. Soc. 76[2] 549-52(1993) (See Table 1 and Fig. 4) which is being submitted herewith. In this article, Moon and Jang teach that the piezoelectric constant $d_{33}$ of the piezoelectric specimen varies in direct response to the oxygen concentration, i.e., it increases as the partial pressure of oxygen in the sintering atmosphere is increased and decreases as the partial pressure is decreased. See, e.g. particularly Table 1 and Figure 4.

The record in this case clearly establishes that those skilled in the art would expect a lead perovskite piezoelectric ceramic material to have a deteriorated piezoelectric d constant if sintered in a reduced oxygen atmosphere. The fact that the deterioration can be combated by employing a ceramic whose A and B site stoichiometric amounts have been altered is not taught or suggested and is surprising and unexpected. Accordingly, withdrawal of this rejection is respectfully solicited.

Claims 1, 4, 5 7-11 and 14-17 have also been rejected under 35 U.S.C. over Horikawa '328 in view of Ponomarev, Horikawa '408 and JP '433. This rejection is also respectfully traversed.

The Horikawa '328 reference has been cited to show co-sintering of a structure having laminated green piezoelectric ceramic and internal electrode layers. There is no disclosure of altering the stoichiometry of the perovskite or sintering in a reduced oxygen atmosphere. The Ponomarv and Horikawa '408 references have been discussed above.

JP '433 teaches that a hard piezoelectric ceramic having silver electrodes in which the diffusion of silver into the ceramic is reduced by sintering at an oxygen density of 1-10 percent. Note that the composition of the ceramic is stoichiometric.

This combination of references suffers from the same deficiencies discussed in the prior art rejection. The hypothesized combination would not be made since it is well known that sintering a lead perovskite piezoelectric ceramic under low oxygen conditions would result in a deterioration of the piezoelectric d constant. In response, the Examiner has stated that JP '433 teaches that sintering in a reduced oxygen atmosphere to reduced diffusion of the silver into the ceramic still results in an excellent piezoelectric property. In response, Applicants respectfully point out that the reference teaches that this result is achieved by insuring the stoichiometric amounts are maintained, either by conducting sintering in a sealed atmosphere to prevent lead loss, or adding extra lead to make the lead content in the A site fall in a particular range. In this connection, see paragraph [0025] in either the machine translation or the more understandable translation attached hereto. There is no teaching or suggestion that the piezoelectric d constant deterioration can be effected by increasing the B site amount above stoichiometric. Accordingly, the finding that increasing the average valence of the B site so that it is greater than 4 but less than 4.1 can be employed to combat the deterioration of the piezoelectric d constant is surprising and unexpected and this rejection should be withdrawn.

Claim 6 and 21 were rejected under 35 U.S.C. Section 103 over the same combination of references in further combination with Feltz. This additional reference has been cited only to teach that it is possible to do partial substitution of the ions in the B position of the perovskite but not to overcome the deficiencies in the prior combinations of references discussed. Accordingly, the further combination of these references with Feltz cannot render the invention obvious.

Claims 12 and 13 were rejected under 35 U.S.C. 103 over the references applied to claim 12 and in further combination with JP '035. The additional Japanese

reference has been cited only with regard to the internal electrodes and not to overcome

the basic deficiencies in the base combination of references. It does not do so and

withdrawal of this rejection is respectfully solicited.

In light of all of the foregoing, it is respectfully submitted that this application

is now in condition to be allowed and the early issuance of a Notice of Allowance is

respectfully requested.

Dated: October 26, 2005

Respectfully submitted,

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JP H11-163433

Translation of [0025]

[0025] Since Pb has a low melting point, it [tends to] spatters and is lost. Because of that, [the amount of] Pb is not stoichiometrically enough to give sufficient sintering to the piezoelectric ceramic, leading to a lowered sintering density and an increased proportion of air-holes and, therefore, unable to give sufficient mechanical strength and [good] piezoelectric characteristics for a piezoelectric transformer. To prevent this, to a certain degree, it is possible to seal off [the piezoelectric ceramic] using a sintering tool, such as a setter, so that the sintering can be performed in the [sealed] environment where Pb hardly spatters; however, it is preferable to add Pb in excess so that (x-y) of [the formula] $(Pb_{x-y}M_y)(Zr_zTi_{1-z})O_3$ is set to $0.955 \leq (x-y) \leq 0.980$ and x is set to $1.005 \leq x \leq 1.030$, and y is set to $0.01 \leq y \leq 0.10$, thereby compensating the amount of Pb, which will be lost, so that Pb is not stoichiometrically deficient and, thus, the reduction of density and the increase of proportion of air holes of the piezoelectric ceramic can be prevented.

# Effects of Sintering Atmosphere on Densification Behavior and Piezoelectric Properties of Pb(Ni$_{1/3}$Nb$_{2/3}$)O$_3$–PbTiO$_3$–PbZrO$_3$ Ceramics

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Densification of polycrystalline Pb(Ni$_{1/3}$Nb$_{2/3}$)O$_3$–PbTiO$_3$–PbZrO$_3$ (PNN–PT–PZ) specimens was enhanced as the partial pressure of O$_2$ in the sintering atmosphere was increased. This observation was attributed to the increase in the internal pressure of a closed pore due to the thermal decomposition of PbO at a low partial pressure of O$_2$. The relative dielectric permittivity ($\varepsilon_r$), $d_{33}$, $k_p$, and grain size of sintered specimens were also increased as the partial pressure of O$_2$ in the sintering atmosphere was increased. The observed dependence of piezoelectric properties on the partial pressure of O$_2$ was discussed in terms of the enhanced formation of the A-site vacancy ($V''_{Pb}$) or the suppression of the B-site defect ($V_O^{··}$) as the oxygen potential increased.

## I. Introduction

IT IS well-known that densification behaviors of oxide ceramics are greatly influenced by sintering atmospheres.[1-3] In general, densification under the atmosphere of a soluble gas such as O$_2$ and H$_2$ produces polycrystalline oxide specimens having near full density.[1] On the other hand, it is very difficult to obtain dense sintered specimens under the atmosphere of an insoluble gas (e.g., N$_2$, Ar, He). Densification of polycrystalline oxide ceramics can be further enhanced by sintering to the closed-pore stage under the atmosphere of a soluble gas and by subsequent switchover to an insoluble (or nondiffusive) gas. The change of sintering atmosphere then builds up a concentration gradient of diffusive gas between the closed pore and the outside atmosphere. This facilitates the outwards diffusion of soluble gas from the closed pore, thus enhancing the shrinkage rate of the closed pore.

In the case of Pb-based electroceramics, thermal decomposition and evaporation of PbO, in general, deteriorates the sintering characteristics, the microchemistry of the specimen, and electrical properties. The thermal decomposition process can be represented as[4-6]

$$PbO(s) \underset{K_1}{\rightleftarrows} PbO(g) \underset{K_2}{\rightleftarrows} Pb(g) + \tfrac{1}{2}O_2 \qquad (1)$$
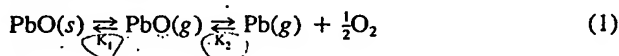
Therefore, the thermal decomposition reaction during the final stage of sintering increases the pressure inside a closed pore and inhibits pore shrinkage. This can be expressed as

$$P_{in} = \frac{2\gamma_{sv}}{r} + P_{therm} \qquad (2)$$

where $P_{in}$ is the internal pressure of the closed pore, $\gamma_{sv}$ is the solid grain/vapor interface free energy, $r$ is the radius of the closed pore, and $P_{therm}$ is the gas pressure generated in the closed

pore. $P_{therm}$ comprises the contribution due to the gas molecules produced by the thermal decomposition reaction. Considering the thermal decomposition reaction represented by Eq. (1), one can predict that the decomposition of PbO is suppressed by sintering in O$_2$ atmosphere. Thus, like Si$_3$N$_4$, which undergoes a thermal decomposition during sintering,[7] the sintering of Pb-based ceramics is expected to be sensitive to sintering atmosphere.

In the case of Pb-based piezoelectric ceramics (e.g., lead zirconate titanate, PZT), sintering atmosphere not only affects densification behaviors but also influences piezoelectric properties. The dissolution/liberation equilibrium of O$_2$ in a solid solution having the perovskite structure can be represented by the following defect equations:

$$\tfrac{1}{2}O_2 = O_O + V''_{Pb} + 2h^· \qquad (3)$$

$$O_O \rightleftarrows \tfrac{1}{2}O_2 + V_O^{··} + 2e' \qquad (4)$$

Therefore, sintering in O$_2$ atmosphere enhances the formation of the A-site vacancy ($V''_{Pb}$) in the perovskite structure (Eq. (3)), increasing the dielectric constant, elastic compliance, and the piezoelectric coupling factor ($k_p$) of the sintered specimen.[8] On the other hand, sintering in N$_2$ atmosphere (or low partial pressure of O$_2$) leads to the enhanced formation of the B-site vacancy (or O-vacancy). The O-vacancy ($V_O^{··}$ in Eq. (4)) increases the mechanical quality factor ($Q_m$), the coercive field, and inhibits grain growth. Therefore, O$_2$ atmosphere acts practically as a donor substituent (softener), whereas N$_2$ atmosphere acts as an acceptor dopant (hardener).

In view of the facts discussed above, the main purpose of the present study was to enhance the densification rate and to adjust the piezoelectric properties of Pb-based perovskite ceramics by controlling the sintering atmosphere. The system that we have chosen is Pb(Ni$_{1/3}$Nb$_{2/3}$)O$_3$–PbTiO$_3$–PbZrO$_3$ (PNN–PT–PZ) pseudoternary solid solution,[9] which is one of the prime candidates for ceramic microactuator materials.

## II. Experimental Procedure

The composition of PNN–PT–PZ solid solution used in this study was Pb$_{0.98}$Cd$_{0.02}$(Ni$_{1/3}$Nb$_{2/3}$)O$_3$–3{Pb$_{0.98}$Cd$_{0.02}$(Zr$_{0.48}$Ti$_{0.52}$)O$_3$} (abbreviated as PNN–3PZT hereafter). Unless specified elsewhere, 0.1 wt% SiO$_2$, 0.3 wt% MnO, and 3 wt% excess PbO were added to this composition as sintering additives and dopants.[10] In the fabrication of the PNN–3PZT specimen, all the constituent metal oxide powders were mixed by ball-milling in a hexane with ZrO$_2$ media for 12 h. The mixed slurry was dried and calcined in a covered alumina crucible at 750°C in air for 3 h. The calcined powder was reground with ZrO$_2$ media for 24 h and dried. The dried powders were first pressed as disks (10 mm in diameter) and then cold isostatically pressed under 190 MPa pressure. The pellets were sintered either at 1050° or at 1100°C, using various sintering atmospheres (N$_2$, air, and O$_2$). The sintered pellets were analyzed by XRD (DMAX-3B, Rigaku, Tokyo, Japan), using CuK$\alpha$ radiation and by scanning electron microscopy (S-570, Hitachi, Tokyo, Japan).

C. D. Near—contributing editor

Samples for dielectric measurements were prepared from sintered pellets by polishing the faces with 6-μm and then 1-μm diamond paste and electroding with silver paint. The silver-coated specimens were heat-treated at 590°C for 15 min and subsequently poled with an electric field of 4 kV/mm at 120°C. Dielectric measurements were performed using an impedance/gain-phase analyzer (Model 4194A, Hewlett-Packard). Capacitance, relative dielectric permittivity ($\varepsilon_r$), tan $\delta$, and resonance/antiresonance frequency were measured at 1 kHz, and the mechanical quality factor ($Q_m$) and the piezoelectric coupling factor ($k_p$) were calculated using these values.

### III.   Results and Discussion

The XRD pattern of the PNN–3PZT specimen (Fig. 1) sintered at 1050°C in air for 3 h shows a coexistence of tetragonal and rhombohedral phases, indicating that the composition of the morphotropic phase boundary (MPB) for the PNN–3PZT system is $ZrO_2:TiO_2 = 0.48:0.52$. The result suggests that the MPB shifts to a Ti-rich region when $Pb(Ni_{1/3}Nb_{2/3})O_3$ (PNN) is added to the PZ–PT system. The temperature dependence of dielectric permittivity of the PNN–3PZT specimen indicated that the Curie temperature ($T_c$) is 257°C and is lower by approximately 130°C than that of PZT specimen having the MPB composition, i.e., $Pb(Zr_{0.52}Ti_{0.48})O_3$.[8]

The density of the sintered specimen as a function of firing time shows that both the initial densification rate and the final sintered density (at 1050°C for 4 h) of the PNN–3PZT specimen increase as the partial pressure of $O_2$ in the sintering atmosphere increases (Fig. 2). As can be noticed from Eq. (1), the thermal decomposition of PbO(s) is suppressed as the partial pressure of $O_2$ increases. Considering the stoichiometry of the decomposition reaction (Eq. (1)), one can write the following relationship for the gas pressure inside a closed pore:

$$P_{therm} = \{PbO(g)\} + \tfrac{3}{2}\{Pb(g)\} + P_0 \qquad (5)$$

where $\{Pb(g)\}$ denotes the pressure increment due to $Pb(g)$ generated by the thermal decomposition, and $P_0$ stands for the atmospheric pressure ($= 1$ atm). Equation (5) holds regardless of sintering atmosphere. Then, one can derive the following relationship between $P_{therm}$ and the partial pressure of $O_2$ using Eqs. (1) and (5):

$$P_{therm} = K_1[1 + \tfrac{3}{2}K_2\{O_2\}^{-1/2}] + P_0 \qquad (6)$$

The above equation predicts that increasing the partial pressure of $O_2$ decreases the internal pressure in a closed pore, enhancing the rate of pore shrinkage (Fig. 2). Besides, since $N_2$ is essentially a nondiffusive gas in metal oxides, the final sintered
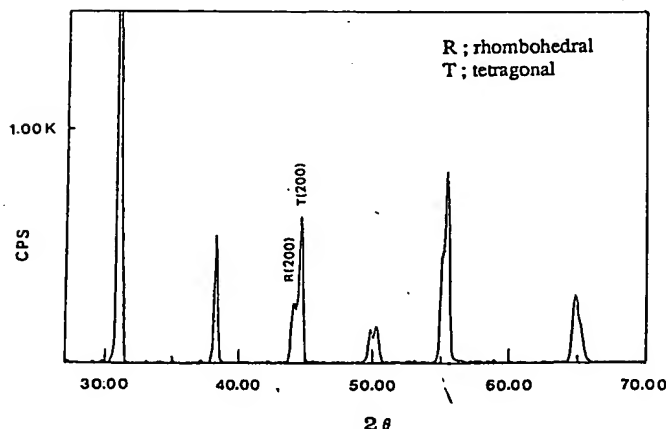
density (closed-pore stage) is expected to be decreased as the partial pressure of $N_2$ in the sintering atmosphere is increased. The result shown in Fig. 2 is consistent with this prediction.

The specimen sintered in either $N_2$ or air atmosphere also showed closed pores associated with nondiffusive $N_2$ gas trapped during the final stage of sintering. Polished microstructures of the sintered specimens (Fig. 3) indicate that $N_2$ atmosphere reduces the rate of grain growth. As discussed previously (Eq. (4)), $N_2$ atmosphere during sintering acts as an acceptor dopant and enhances the formation of the O-vacancy. The O-vacancy tends to shrink the cell size, and this lattice shrinkage, in turn, suppresses grain growth.[8]

Table I shows piezoelectric properties of the PNN–3PZT specimen (with 0.1 wt% $SiO_2$ and 0.3 wt% MnO) sintered at 1050°C for 2 h using various atmospheres. $O_2(1\ h) \rightarrow N_2(1\ h)$ in Table I, for example, designates sintering in $O_2$ atmosphere for 1 h, followed by a second sintering in $N_2$ atmosphere for another 1 h. As shown in the table, the relative dielectric permittivity ($\varepsilon_r$) of the PNN–3PZT specimen increases as the partial pressure of $O_2$ in the sintering atmosphere increases, indicating a donor (softener) effect of $O_2$ in the Pb-based perovskite structure. The result also shows that switching the sintering atmosphere of air to $N_2$ in the middle of sintering decreases $\varepsilon_r$ by ~200 (i.e., 1704 vs 1508). Similarly, conversion of $O_2$ atmosphere to $N_2$ atmosphere reduces $\varepsilon_r$ by ~230, showing an acceptor effect of $N_2$ in the PNN–PT–PZ solid solution. As shown in Table I, essentially the same type of correlation was found for $d_{33}$ of the PNN–3PZT specimens sintered using various atmospheres. On the other hand, $Q_m$ increases significantly as the partial pressure of $N_2$ increases, again demonstrating the role of $N_2$ atmosphere as a hardener. As shown in Table I, switching $O_2$ atmosphere to $N_2$ atmosphere in the middle of sintering increases the value of $Q_m$ by ~200 (177 vs 372).

Since the PNN–3PZT specimens contain 0.3 wt% MnO (together with 0.1 wt% $SiO_2$), the effects of sintering atmosphere discussed in the previous paragraph are possibly
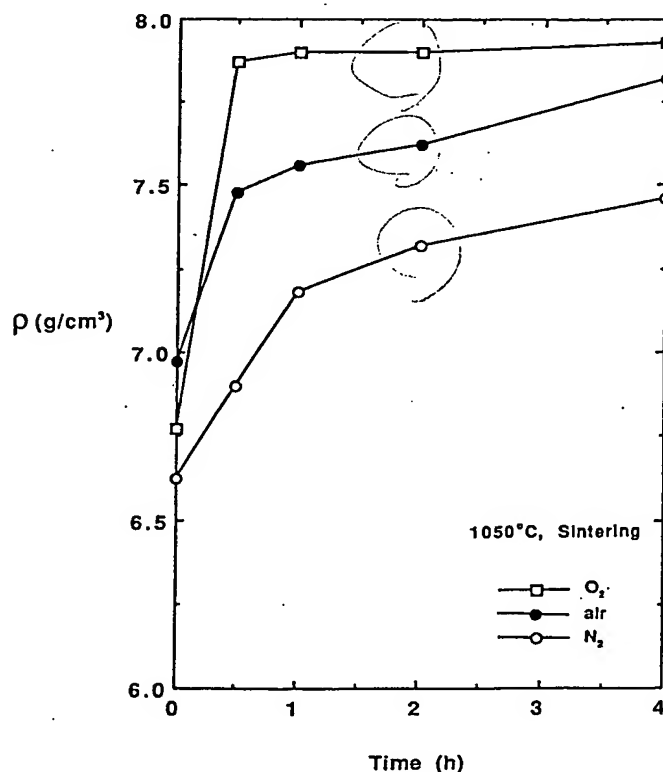
**Fig. 1.**   XRD pattern of PNN–PT–PZ (PNN–3PZT) specimen sintered at 1050°C for 3 h, showing a coexistence of tetragonal and rhombohedral phases.

**Fig. 2.**   Sintered density of PNN–PT–PZ specimens as a function of firing time at 1050°C. The specimens were sintered using three different atmospheres ($O_2$, $N_2$ and air).
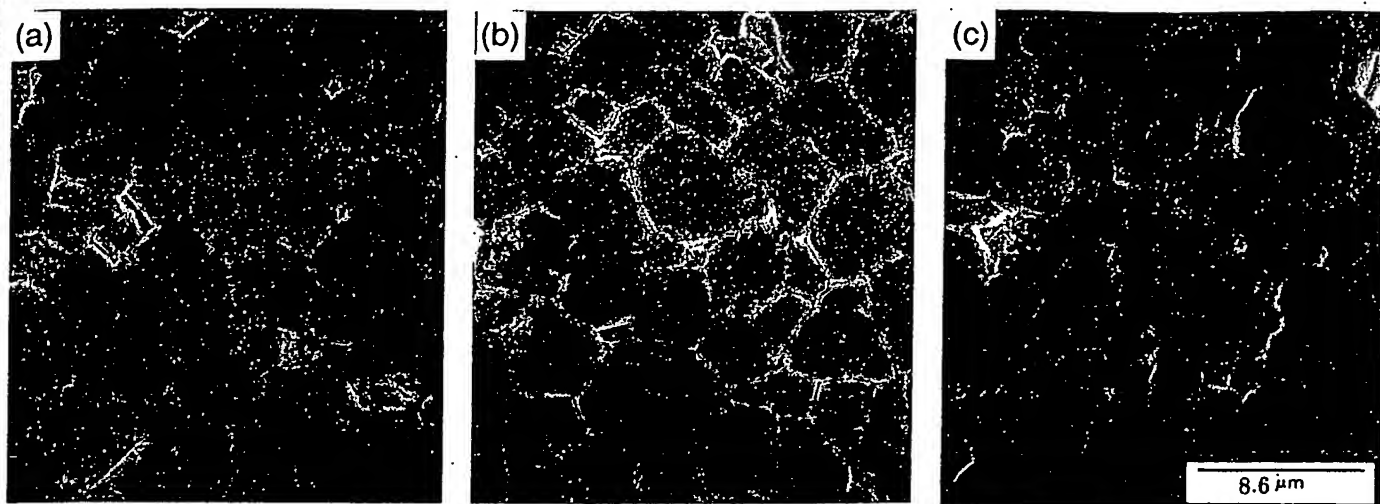
**Fig. 3.** Polished microstructures of PNN–PT–PZ specimens sintered at 1050°C for 2 h in (a) air, (b) $O_2$, and (c) $N_2$ atmospheres.

obscured by the dissolution/reduction of the transition metal element, Mn, in the perovskite structure. To clear up this ambiguity, the extent of the pure atmospheric effect (i.e., partial pressure of $O_2$) on the piezoelectric properties of the PNN–PT–PZ system was examined by measuring $d_{33}$ and $Q_m$ of the sintered specimens in the absence of MnO. Figure 4 shows $Q_m$ and $d_{33}$ values of the PNN–3PZT specimens (sintered under three different atmospheres) as a function of the amount of MnO added during the fabrication stage. In contrast to the PNN–3PZT specimens discussed previously (Figs. 1–3 and Table I), all the specimens corresponding to Fig. 4 were prepared without the addition of $SiO_2$. It was observed that excluding $SiO_2$ in the PNN–3PZT specimen retards densification significantly. Therefore, sintering without the addition of $SiO_2$ was done isothermally at a higher temperature (1100°C for 3 h vs 1050°C for 2 h). As shown in Fig. 4, the specimens prepared without MnO clearly demonstrate a donor effect of $O_2$ (or an acceptor effect of $N_2$) in the perovskite structure, supporting the previous conclusion.

$Q_m$ increases gradually as the amount of MnO added to the system increases, while $d_{33}$ decreases monotonously in the presence of oxygen (air or $O_2$ atmosphere). This indicates an acceptor effect of Mn oxide in the PNN–PT–PZ system. It has been reported[11,12] that $Mn^{3+}$ ions enter the B-sites of the perovskite structure in PT ($PbTiO_3$) and PZT ceramics sintered in air atmosphere. In this case, the charge deficit of $Mn^{3+}$ ions at the B-sites is compensated mostly by oxygen vacancies which pin the walls of ferroelectric domains by local strain. The substitution of $Mn^{3+}$ in the B-sites (e.g., substitution for Ti atom sites) can be represented as

$$Mn_{Ti^{4+}}^{3+} \rightarrow Mn_{Ti}' + \tfrac{1}{2}V_O^{\cdot\cdot}$$ (7)

This predicts an enhanced formation of the O-vacancy by Mn ions in air atmosphere and, thus, explains the above observation.

For a given doping level of MnO, $Q_m$ consistently exhibits a higher value in $N_2$ atmosphere, while $d_{33}$ is significantly reduced (Fig. 4). This clearly demonstrates an additional effect of the sintering atmosphere (i.e., enhanced formation of the O-vacancy via Eq. (4)) for a given doping level of Mn oxide. The mechanical quality factor becomes essentially independent of the partial pressure of $O_2$ at a higher doping level of MnO (~0.7 wt%). This suggests that the substantial effect of Mn species (Eq. (7)) dominates over the atmospheric effect (Eq. (4)) as the content of Mn oxide in the sintered specimen increases. As shown in Fig. 4(b), $d_{33}$ is weakly dependent on the doping level up to 0.5 wt% addition of MnO in $N_2$ atmosphere. This suggests that the dissolution of Mn oxide exerts a minor effect on the piezoelectric constant at low partial pressure of $O_2$. This observation could be attributed to the formation of $Mn^{3+}$ ions at the A-sites of perovskite structure without forming vacancies at low partial pressure of $O_2$.[11] However, the observed rapid increase in $Q_m$ ($N_2$ atmosphere, Fig. 4(a)) in response to the increase in MnO content cannot be explained in terms of this proposition. The apparent anomaly could be solved by assuming that some of the Mn species first oxidize to the trivalent state ($Mn^{3+}$ after the calcination step) and subsequently enter the B-sites (Eq. (7)) during sintering in $N_2$ atmosphere. This is not impossible since, due to the thermal decomposition reaction represented by Eq. (1), a finite amount of $O_2$ exists during sintering, even in $N_2$ atmosphere. However, there is no clear evidence for this hypothesis, and thus it is a subject of future investigation.

It has been found that an optimization of additives (0.5 wt% $SiO_2$ + 0.7 wt% MnO, instead of 0.1 wt% $SiO_2$ + 0.3 wt% MnO) further increases $Q_m$ to 1300, without a significant loss of the piezoelectric constant ($d_{33}$ ~ 350). Since both high $Q_m$ and $d$ values are desirable for a piezoelectric actuator that utilizes a rigid strain (servo driving), the above result suggests that suitably adjusting the sintering atmosphere, in conjunction with an

**Table I. Piezoelectric Properties of PNN–PT–PZ Specimens Sintered at 1050°C for 2 h Using Various Atmospheres**

| Atmosphere | $\varepsilon_r$ | $d_{33}(\times 10^{-12}$ C/N) | $Q_m$ | $K_p(\%)$ | $\tan\delta$ ($\times 10^{-3}$) | $\rho$ (g/cm³) |
|---|---|---|---|---|---|---|
| Air(2 h) | 1704 | 342 | 191 | 52 | 0.95 | 7.62 |
| Air(1 h) → $N_2$(1 h) | 1508 | 335 | 333 | 51 | 0.63 | 7.55 |
| $O_2$(2 h) | 1862 | 368 | 177 | 54 | 0.87 | 7.90 |
| $O_2$(1 h) → $N_2$(1 h) | 1633 | 326 | 372 | 54 | 0.75 | 7.95 |
| $N_2$(2 h) | 1196 | 326 | 380 | 47 | 0.64 | 7.32 |

一般に N₂ 中焼成では
d₃₃ は大幅に低下する。



(a) 1100°C, 3h Sintering
○ air
● O₂
□ N₂

$Q_m$

MnO wt%



(b) 1100°C, 3h Sintering
○ air
● O₂
□ N₂

$d_{33}$ ($\times 10^{-12}$ C/N)

MnO wt%
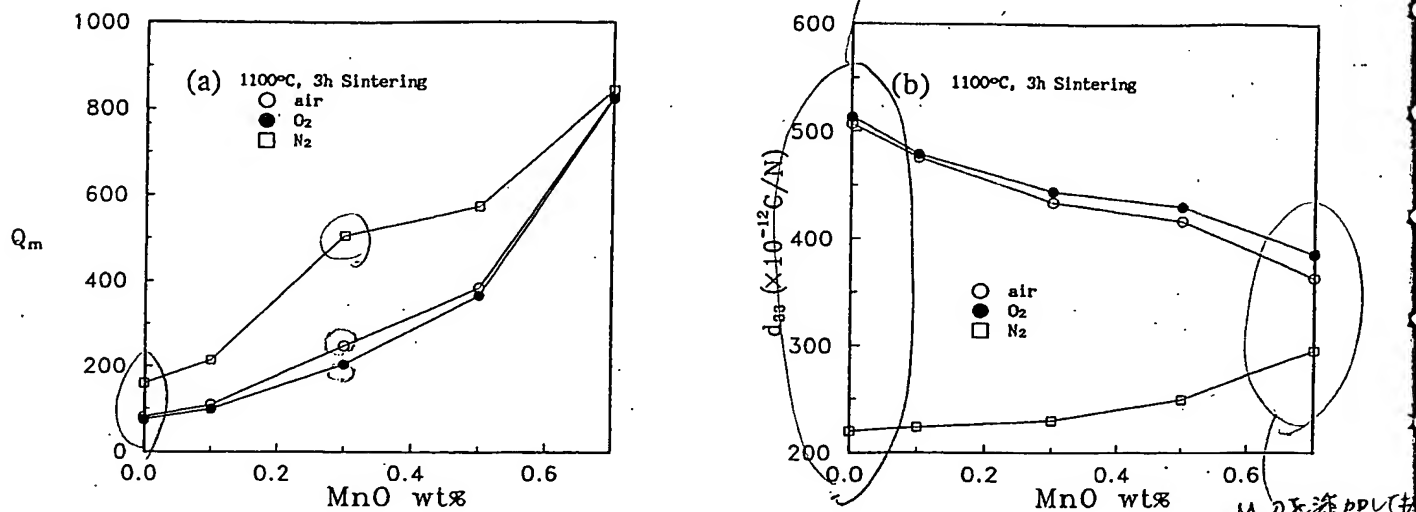
MₐO を添加しても

Air や O₂ 中焼成と
同等の d₃₃ は得られない

Fig. 4. Mechanical quality factor ($Q_m$) and piezoelectric constant ($d_{33}$) vs doping level of MnO for PNN–PT–PZ specimens sintered at 1100°C for 3 h using three different atmospheres.

optimization of dopants, is a useful strategy for the fabrication of piezoelectric ceramic actuators using the PNN–PT–PZ pseudoternary system.

**References**

[1]R. L. Coble, "Sintering Alumina: Effect of Atmospheres," *J. Am. Ceram. Soc.*, **45** [3] 123–27 (1962).

[2]Y.-K. Paek, K.-Y. Eun, and S.-J. L. Kang, "Effect of Sintering Atmosphere on Densification of MgO-Doped Al₂O₃," *J. Am. Ceram. Soc.*, **71** [8] C-380–C-382 (1988).

[3]P. Duran and C. Moure, "Sintering at Near Theoretical Density and Properties of PZT Ceramics Chemically Prepared," *J. Mater. Sci.*, **20**, 827–33 (1985).

[4]D. A. Northrop, "Vaporization of Lead Zirconate–Lead Titanate Materials," *J. Am. Ceram. Soc.*, **50** [9] 441–45 (1967).

[5]D. A. Northrop, "Vaporization of Lead Zirconate–Lead Titanate Materials: II, Hot-Pressed Compositions at Near Theoretical Density," *J. Am. Ceram. Soc.*, **51** [7] 357–61 (1968).

[6]P. Gr. Lucuta, Fl. Constantinescu, and D. Barb, "Structural Dependence on Sintering Temperature of Lead Zirconate–Titanate Solid Solutions," *J. Am. Ceram. Soc.*, **68** [10] 533–37 (1985).

[7]F. F. Lange, "Volatilization Associated with the Sintering of Polyphase Si₃N₄ Materials," *J. Am. Ceram. Soc.*, **65**, C-120–C-121 (1982).

[8]B. Jaffe, *Piezoelectric Ceramics*; Ch. 10. Academic Press, New York, 1971.

[9]E. A. Buyanova, P. L. Strelets, I. A. Serova, and V. A. Isupov, "Ferroelectric Properties of Pb(Ni₁/₃Nb₂/₃)O₃–PbTiO₃–PbZrO₃ Solid Solutions," *Bull. Acad. Sci. USSR, Phys. Ser.* (*Engl. Transl.*), **29**, 1877–80 (1965).

[10]G. Zhilun, L. Longtu, G. Suhua, and Z. Xiaowen, "Low-Temperature Sintering of Lead-Based Piezoelectric Ceramics," *J. Am. Ceram. Soc.*, **72** [3] 486–91 (1989).

[11]D. Hennings and H. Pomplun, "Evaluation of Lattice Site and Valence of Mn and Fe in Polycrystalline PbTiO₃ by Electron Spin Resonance and Thermogravimetry," *J. Am. Ceram. Soc.*, **57** [12] 527–30 (1974).

[12]Y. S. Ng and S. M. Alexander, "Structural Studies of Manganese Stabilized Lead-Zirconate-Titanate," *Ferroelectrics*, **51**, 81–86 (1983). □